

Chapter 1

Introduction

1.1 Solid-state dye lasers

Dye lasers, which make use of organic colorants to produce coherent emissions in the UV to IR spectral region when optically pumped by flashlamps or lasers, operate in the vapour, liquid and solid states. Liquid-state dye lasers are mostly studied as they are conveniently prepared by dissolving the dyes in a suitable solvent. Vapour-phase dye lasers, although more efficient, require high temperature's environment. On the other hand, solid-state dye lasers can be readily prepared by embedding the dye into an appropriate (organic) polymer or (inorganic) sol-gel host, or into a composite of both, to obtain a physically rigid structure (Schäfer, 1990).

With a solid-state dye laser, the compatibility of the host material and the colorant will depend on their chemical structures and the processing procedure. Each family of dyes covers only a limited range, but the host materials for a number of families have yet to be discovered, particularly the matrices for the blue and green dyes. The Fluorescein family, which covers the green region, is incompatible with a

large number of matrices. The problem of dye-host compatibility is multiplied if a combination of dyes is required that spans the visible. More importantly, in terms of operational lifetime, the typical dye in the solid-state system decomposes after a number of pulses.

1.2 Progress in solid-state dye lasers

Among materials used as matrices for laser dyes, poly(methyl methacrylate) (PMMA) is the most popular material owing to its high optical transparency. The polymer is compatible with Rhodamine 6G (R6G), which happens to be a highly efficient dye that has been the most studied. The polymer system derived from R6G which has been dispersed in methyl methacrylate monomer and the mixture then polymerised has been reported to achieve the lifetime of 20,000 shots at a localised lasing spot (Costela *et al.*, 1996). A modified PMMA rod has been reported to give an emission of a positive lasing characteristic (with no additional resonator, index-matching fluid or anti-reflection coating) when excited by a flashlamp (Finlayson *et al.*, 1998). Dye lasers in the form of slabs can be fabricated by a simple hot-press moulding technique, where radical-initiated decomposition of dyes is eliminated (Yee *et al.*, 1998).

Dyes can be incorporated into sol-gel materials, which can be prepared by solution methods at ambient temperatures, either before or after the sol has gelled. Because of their rigidity, sol-gel glasses display structural stability exceeding that of polycom, ormosil and PMMA. Additionally, the dyes cannot be leached from the sol

gel (Rahn & King, 1995). A sol-gel silica has also been fabricated for narrow linewidth operation; the laser beam showed a Gaussian far-field profile with only minor divergence (Lo *et al.*, 1998). Another sol-gel matrix is material showed compatible with Coumarins, but is somewhat less compatible with Pyrromethene and Disodium Fluorescein (DF). Nevertheless, the simultaneous solution of Coumarin and DF in the sol gel has permitted the energy transfer mechanism of the Coumarin/DF pair of dyes to be understood in terms of induced green superradiant emission with DF at a concentration below its lasing threshold (Law *et al.*, 1998).

Materials that have been examined as host materials include poly(carbonate), poly(styrene), polycom and ormosil. These as well as the materials mentioned above furnish solid-state dye lasers in the form of slabs.

Solid-state dye lasers that are fabricated in the form of films or coatings of micron and sub micron thickness exhibit waveguiding properties. Such a system was first reported in 1972 for R6G/polyurethane that is pumped by nitrogen laser (Ulrich & Weber, 1972); the study was later extended to Coumarins into PMMA (Itoh *et al.* 1977). The results of these studies on the performance of the dye molecules as evaluated from measurements of optical gains showed high rates of decay.

Thin film lasers exhibit distributed feedback (DFB) properties owing to gain and refractive index modulation; this property has been demonstrated in a study on a thin-film optical-waveguide that was pumped with spatially modulated radiation (Bjorkholm & Shank, 1972). An apparatus that uses prisms for the lasing of R6G/PMMA had also been reported for which tuning was effected by altering the angle of the film and the pumping radiation (Cheremiskin & Chekhlova, 1974).

Films having a thickness of about 15 μm were investigated of their superradiant emissions when excited that enter the flat glass supports at angles exceeding the critical total reflection angle. Multimode planar waveguide was obtained instead of single mode transmission. At a completely flat edge, two output beams were obtained at a divergence angle; exiting from a side of the supports after undergoing multiple amplifications that are guided within the body of the supports. This study found the efficiency of the superradiant red Perylimide dye doped silica-PMMA composite film dye-laser (as defined by the ratio of output energy/absorb energy) to be 5.4% for the four exiting beams (Shamrakov & Reisfeld, 1993).

PMMA thin-film lasers, prepared by dip coating, have also been studied by using steady-state and time-resolved spectroscopy; 1,1,4,4-tetraphenyl-1,3-butadiene, coumarin-334 and Rhodamine 6G gave single, binary and ternary emissions, the concentrations of the individual dyes being crucial for gain narrowing. As R6G concentration was kept relatively low to avoid dye aggregation, energy transfer from TPB and C334 are needed to enhance the emission. The dye in the film was suggested as a probe for film thickness. (Huang *et al.*, 1999).

1.3 Photostability

The stability of the dye molecules in the solid-state host medium has been examined over the years. Although various dyes degrade in different manners, the mechanisms themselves can be generalised into several primary factors (which include thermal destruction during fabrication or upon irradiation, chemical interaction of the dye molecules and macromolecules, and viscosity of the host medium) and external factors (such as pumping energy and the pumping rate).

The photostability of dyes in modified PMMA is defined by the bleaching efficiency $\Psi = D_o / D$, which is the ratio of the optical density of the dye in the initial state versus that of the bleached state. Low values are attributed to the aggregation of dye molecules into dimers, trimers and oligomers, particularly when the dye dissolves only sparingly in PMMA. The dye can also be excited to form free radicals, which then react with neutral molecules. Ideally, free radicals and their reaction products should be absent (Dyumaev *et al.*, 1992).

Lasing efficiency, and consequently stability, are raised if structurally rigid matrices constitute the host as the free volume of the polymer is reduced. Structural rigidity can be attained through crosslinking of the polymer chains; at an optimum degree of crosslinking, internal rotation of the dye is severely restricted, so that the absorbed energy is not lost by non-fluorescent pathways (Amat-Guerri *et al.*, 1993).

The one-photon photodestruction model of photostability has been tested by comparing the experimentally derived average number of photons absorbed by each molecule before being destroyed with calculated values. The study noted that dyes are

more stable in sol gel matrices than in solution; explained by the isolation of dye molecules from the reactive impurities and the reduction in thermally excited reaction because of rigidity of the matrices and strong interactions with organic dopants (Dubois *et al.*, 1996).

The photostability arising from a change from the low-viscosity liquid state to the solid state (i.e., PMMA) was analysed by following the dependence of induced fluorescence and the output energy. Lasing efficiency was found to decrease with increasing viscosity, which was also accompanied by an increasing fluorescence lifetime; photobleaching gave decomposition products that absorbed at laser emission wavelengths and the photothermal reaction gave molecules were decomposed by heat (Costela *et al.*, 1998).

The influence of the pump repetition rate on photostability was investigated in a study on optically pumped PMMA. The study showed that chemical reactions of the dye in the excited state rather than thermal decomposition was the main cause of photodegradation (Popov, 1998).

1.4 Current project

The laser dyes Coumarin 460 (C460), Disodium Fluorescein (DF) and Rhodamine 640 perchlorate (R640) emit in the red, green and blue of the visible spectra. Their wavelength correspondence with the primary colours of the International Commission of Illumination (CIE) (MacAdam, 1985) is shown in Table 1.1. The dyes, if they can be combined, will cover a much wider range. On the other hand, poly(vinyl alcohol) (PVA), is a polymer whose optical properties parallel closely those of PMMA, and a limited number of investigations have demonstrated the capability of this polymer to entrain dyes by hydrogen-bonding interactions. These studies (Pritchard, 1973), as well as studies on the application of photosensitised dyes in PVA (Couture, 1991; Lessard *et al.*, 1993; Egami *et al.*, 1997), make no mention of the lasing ability of the dyes.

Dye	Lasing wavelength (nm)	<i>CIE 1931 data</i>	
		Wright's primaries	Guild's primaries
Coumarin 460 (Coumarin 1, Coumarin 47)	440-478	460	459, 464
Disodium Fluorescein	530-568	530	535, 543
Rhodamine 640 perchlorate (Rhodamine 101)	620-665	650	628, 630

Table 1.1 The dyes and the corresponding wavelength of the common CIE primaries.

The present project uses PVA as the host material for three identified dyes that show high efficiency in solution. The lasing action of the solid-state film dye-lasers is examined with Transversely Excited Atmospheric (TEA) and Transversely Excited (TE) nitrogen lasers, and the laser performances of the film dye-lasers are evaluated on the basis of the spectral features, efficiencies, dye photostability, beam characteristics and input power.